Differentiation of Lipsticks by Raman Spectroscopy

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Abstract

Dispersive Raman spectra have been obtained using a Raman microscope and an excitation wavelength of 632.8 nm from 69 lipsticks of various colours and from a range of manufacturers without any pre-treatment of the samples. 10% of the samples were too fluorescent to give Raman spectra. 22% of the samples gave spectra which were unique to the brand and colour within the collected sample set. The remaining 68% of the samples gave spectra which could be classified into seven distinct groups. Discrimination of red lipsticks by this technique was the most difficult. The spectra of deposited lipstick samples remained unchanged over a period of a least a year.

Keywords: Raman spectroscopy, lipsticks, trace evidence.

Introduction

Identifying and establishing of the source of trace evidence in forensic science is an important task. There are many types of trace evidence that can be encountered by a forensic scientist at a crime scene, and one of these is cosmetic evidence such as lipstick smears. Lipsticks can easily be transferred and, like other forms of evidence, they can provide a link between a suspect and a victim, as well as between individuals and a crime scene. Lipsticks can be found as smears on a variety of surfaces such as glass, cigarette butts, garments, paper and miscellaneous crime scene surfaces.

Identification of, and differentiation between, lipstick samples can make an important contribution to a forensic investigation.

Although the exact composition of lipsticks varies between manufacturers, the majority of lipsticks have similar compositions. They contain oils, waxes, pigments, antioxidants, preservatives and perfumes. Most of the matrix of a lipstick is composed of a mixture of emollients such as castor, vegetable, mineral and lanolin oils (typically 40%-70%) and waxes such as beeswax or carnauba (typically 8%-15%). Water-insoluble organic dyes (such as erythrosine, amaranth, rhodamine, tartrazine, dibromofluorescein, tetrabromo-fluorescein) and inorganic pigments (especially titanium dioxide and iron oxides) are used as colourants (typically 0.5%- 8%). Water-soluble dyes are "laked" (i.e. combined with metal oxides) to form insoluble precipitates which are then suspended in the oil base of the lipstick. These colourants are categorised by their colour index (CI) numbers (e.g. C.I.77491 for iron (III) oxide) [1-3].

Several methods for the forensic examination of lipsticks have been reported in which the sample masses are typically less than 1 mg. For example, one study considered 117 lipsticks and found good discrimination could be obtained by first visually comparing their colours [4]. If the samples were found to be indistinguishable, energy dispersive X-ray analysis was carried out. If no significant difference in elemental composition was observed, then the colour additives were examined by thin-layer chromatography (TLC). Finally if discrimination was still not observed the samples were analysed by high performance liquid chromatography (HPLC). A further study involving over 300 lipstick samples found that TLC and gas chromatography were suitable for the analysis, characterisation and discrimination of small quantities of lipstick found in casework [5]. The combination of microspectrophotometry and scanning electron microscopy/energy dispersive spectroscopy has also been found to be an effective combination for characterising colour and elemental composition [6]. Elemental analysis data can also be obtained from neutron activation analysis using γ-ray spectrometry [7]. Another successful combination of techniques is fluorescence observation and purge-and-trap gas chromatography [8].

These techniques have some disadvantages. Some involve human opinion (e.g. microscopy) and some are destructive involving extraction processes. Ideally the analysis should be performed non-destructively on trace amounts of samples with the minimum of sample preparation and the avoidance of contamination. Raman spectroscopy is an easy, rapid and non-destructive method which requires no sample preparation and can analyse samples contained in evidence bags [9]. The unique vibrational spectra of molecules results in a high degree of confidence in identification. Surprisingly little has been published concerning the Raman spectroscopy of lipsticks. Surface enhanced resonance Raman spectroscopy has been used for the *in-situ* characterisation of chromophores in six red lipstick smears on glass and cotton surfaces [10,11] and dispersive Raman spectroscopy gave chemical fingerprints from four (damson, champagne, pink frost and mango) lipsticks [12].

Experimental

The experiments were carried out using a Jobin-Yvon 640 micro-Raman spectrometer utilising a Uniphase (model 1145) helium-neon laser operating at a wavelength of 632.8 nm. It incorporated a liquid-nitrogen cooled charge coupled device (CCD) detector. The laser had a fixed output of 35 mW and the laser power at the sample was 4mW. A x100 objective lens was used giving a beam diameter of about 1 µm. The spectrometer was calibrated against the silicon line at 520.6 cm^{-1}. Each lipstick was smeared onto a glass microscope slide and five spectra were obtained from different parts of each sample to check for homogeneity. Depending on the quality of the spectra 40 to 100 accumulations of 0.5 to 4 seconds were used. The difference in these parameters only served to improve the signal-to-noise ratio of the spectra and did not have any effect on the presence/absence and positions of peaks. Spectra were exported to Labspec version 5 for processing, analysis and presentation.

A total of 69 lipsticks from 10 different brands were analysed. These included Almay 36, Bourjois (No's. 15, 16, 32, 54), L'Oreal (No's. 164, 243, 524, 900), Revlon (No's. 07, 46, 455, 675), Elizabeth Arden 17, Max Factor (No's. 30 and 210) and La Femme 29 which were purchased online at www.cosmetics4less.net; and Barry M (No's. 52, 53, 54, 62, 101, 117, 113, 121, 140, 141, 144, 145, 146), Prestige (CL93A, CL78A, PL28A, PL38A, PL49A), Revlon (No's. 004, 005, 006, 008, 009, 020, 025, 030, 035, 045, 075, 080, 090, 095, 103, 353, 359, 371, 430, 450, 663, 750); and UNE lipsticks (L02, L05, L07, L09, S03, S05, S07, S08, S12, S15, S17, S19) which were obtained from the local Boots store in Canterbury, Kent.

To identify the peaks of the lipstick spectra, some of the common ingredients used in the manufacture of lipsticks were also obtained and analysed. These included beeswax, castor oil, carnauba wax, and FD&C Yellow No. 6 Aluminium lake (Sunset Yellow) dye which were purchased from Sigma-Aldrich; and FD&C Yellow No. 5 Aluminium lake (tartrazine) dye and FD&C Blue No. 1 (erioglaucine disodium salt) dye which were purchased from Acros Organics.

Results and Discussion

The majority of lipsticks analysed in this study appeared heterogeneous under the microscope at x100 magnification power, so Raman spectra from five different positions of each sample were obtained to gauge the inhomogeneity. In all cases the peak positions were the same within +/- 4 cm^{-1}, but there was variability in the relative intensities. Representative spectra are presented in the figures.

Table 1 Lipsticks Grouped by their Discrimination by Raman Spectroscopy

Group	Brand	Prod #	Main Colour	Shade/Comment
1	Almay	36	Red	
1	Barry M	145	Pink	Dark
1	Barry M	121	Red	
1	Bourjois	15	Pink	
1	Bourjois	16	Red	
1	Bourjois	54	Red	
1	Bourjois	32	Red	Dark
1	L’Oreal	900	Brown	Pink
1	L’Oreal	164	Red	Light
1	Prestige	CL93A	Pink	Very dark
1	Revlon	46	Brown	
1	Revlon	095	Red	Very dark
1	Revlon	009	Red	Matt, brown

1	Revlon	030	Pink	Very dark
1	Revlon	430	Pink	Dark, shimmery
1	Revlon	006	Red	Dark
1	Revlon	675	Red	
1	Revlon	090	Red	
1	Revlon	080	Red	Bright
1	Revlon	045	Brown	Dark pink
2	Barry M	146	Pink	
2	Revlon	005	Peach	Red
3	Barry M	53	Orange	Peach
3	Revlon	035	Brown	
3	Revlon	750	Red	Orange
3	Revlon	004	Pink	Dark, peach
3	Revlon	450	Pink	Shimmery
3	Revlon	025	Pink	
4	Revlon	371	Brown	Peach
5	Barry M	52	Pink	
5	Barry M	62	Pink	
6	Barry M	140	Pink	Shimmery
6	Barry M	113	Pink	Shimmery, light
6	Revlon	455	Pink	Shimmery
7	Revlon	353	Brown	Shimmery, light
7	UNE	L02	Brown	
7	UNE	L05	Brown	
7	UNE	L07	Brown	
7	UNE	L09	Brown	
7	UNE	S03	Brown	
7	UNE	S05	Brown	
7	UNE	S07	Brown	
7	UNE	S08	Brown	
7	UNE	S12	Brown	
7	UNE	S15	Brown	
7	UNE	S17	Brown	
7	UNE	S19	Brown	
F	Barry M	144	Pink	Very dark
F	Barry M	141	Burgundy	
F	Elizabeth Arden	17	Brown	Pink
F	L’Oreal	243	Brown	Light, pink
F	Max factor	30	Brown	Lipgloss, pink
F	Max factor	210	Brown	

F	Revlon	663	Violet	Very dark
U	Barry M	101	Flesh	
U	Barry M	54	Orange	Peach
U	Barry M	117	Orange	
U	L'Oreal	524	Brown	
U	La Femme	29	Brown	Pink
U	Prestige	CL78A	Brown	light
U	Prestige	PL28A	Orange	Peach
U	Prestige	PL38A	Brown	Very light
U	Prestige	PL49A	Brown	Pink
U	Revlon	008	Brown	
U	Revlon	359	Brown	
U	Revlon	07	Brown	
U	Revlon	075	Peach	
U	Revlon	020	Pink	Shimmery
U	Revlon	103	Brown	Shimmery

F = fluorescent, U = gives unique spectrum

Seven samples were too fluorescent (denoted as Group F in Table 1) to obtain spectra from and hence 62 lipstick spectra were obtained, although most lipsticks produced spectra with a fluorescent baseline.

Fifteen lipsticks gave unique spectra each of which could be readily discriminated from the other 61 samples (denoted as Group U in Table 1) by visual inspection of the spectra. Fig. 1 compares the spectra of four of these lipsticks. The remaining 47 lipsticks gave Raman spectra that could be divided into seven distinct groups which could be distinguished from the other groups as shown in Table 1. Some groupings relate closely to the colour or brand of the lipstick (e.g. Group 7 contains exclusively brown lipsticks mainly by UNE), but other groups contain a range of colours (e.g. Group 3) or brands (e.g. Group 1).

Spectra of five pink lipsticks are shown in Fig. 2. Bourjois 15 and Revlon 025 have similar spectra in the region 200-1800 cm^{-1} and are also similar to lipstick spectra previous reported using SERRS at 514.5nm excitation [10]; but are clearly distinguishable from Barry M 52, Revlon 020 and Barry M 133, which are all distinguishable from each other. Spectra c)-e) also clearly show the presence of titanium oxide in the form of anatase. Fig. 3 compares the Raman spectra of two lipsticks with that of anatase.

Spectra of four orange lipsticks are displayed in Fig. 4. Clear differences can be seen between the three Barry M products, but Revlon 750 is very similar to Barry M 53 and cannot be differentiated. Spectra of four brown lipsticks are displayed in Fig. 5 and show clear differences within (Revlon) and between brands (Revlon and UNE).

Red lipsticks were the most challenging to differentiate using this form of Raman spectroscopy and almost all appear in Group 1 regardless of manufacturer. Fig. 6 compares the Raman spectra of Bourjois 16, a typical Group 1 lipstick, with Revlon 080 which, although similar and placed in Group 1, has small reproducible differences. These results suggest a range of manufacturers use similar formulations for red lipsticks. The spectra are similar to the previously reported SERRS of red lipsticks [10].

Some components of lipsticks were also analysed using the same spectrometer. Castor oil and carnauba wax gave very fluorescent spectra with no discernible features and may be contributing to the fluorescence in many cases. Beeswax on the other hand produced a spectrum with a flat baseline and well defined peaks, which are observed in the spectra of some lipsticks. For example, Fig. 7 compares the spectra of beeswax and Barry M 140.

Raman spectra of several dyes were obtained and many gave fluorescent emissions with no discernible spectral features to contribute to the lipstick spectra, which may explain the lack of dependence on colour in some cases; whereas others such as FD&C Yellow No. 5 Aluminium Lake (tartrazine) had characteristic peaks. Dyes are present in lipsticks in relatively small amounts (approximately 0.5% - 8%) [1], so unless a resonance effect is observed due to a UV-visible absorption band in the dye which would result in an increased Raman signal, then the intensity contribution from dyes is small. Fig. 8 illustrates the spectra of three dyes.

Lipstick smears are persistent and there is no literature pertaining to the effect of aging on the Raman spectra of lipsticks, thus it is forensically important to analyse old samples. For this purpose, several samples were deposited on glass slides and left on a bench in the laboratory, and had their spectra taken periodically. No changes were observed over the course of more than one year. Fig. 9 depicts the Raman spectra of Rimmel 080 at three time intervals.

Conclusions

In many cases Raman spectra of lipsticks can be obtained with 632.8 nm excitation frequency without the use of SERS or SERRS hence avoiding any pre-treatment of potential evidence. Although the red lipsticks studied gave very similar spectra, for many other colours and for several brands there was often significant discrimination which could allow the presence or absence of a particular lipstick to be determined. The spectra of deposited lipsticks appeared unchanged over a course of at least a year.

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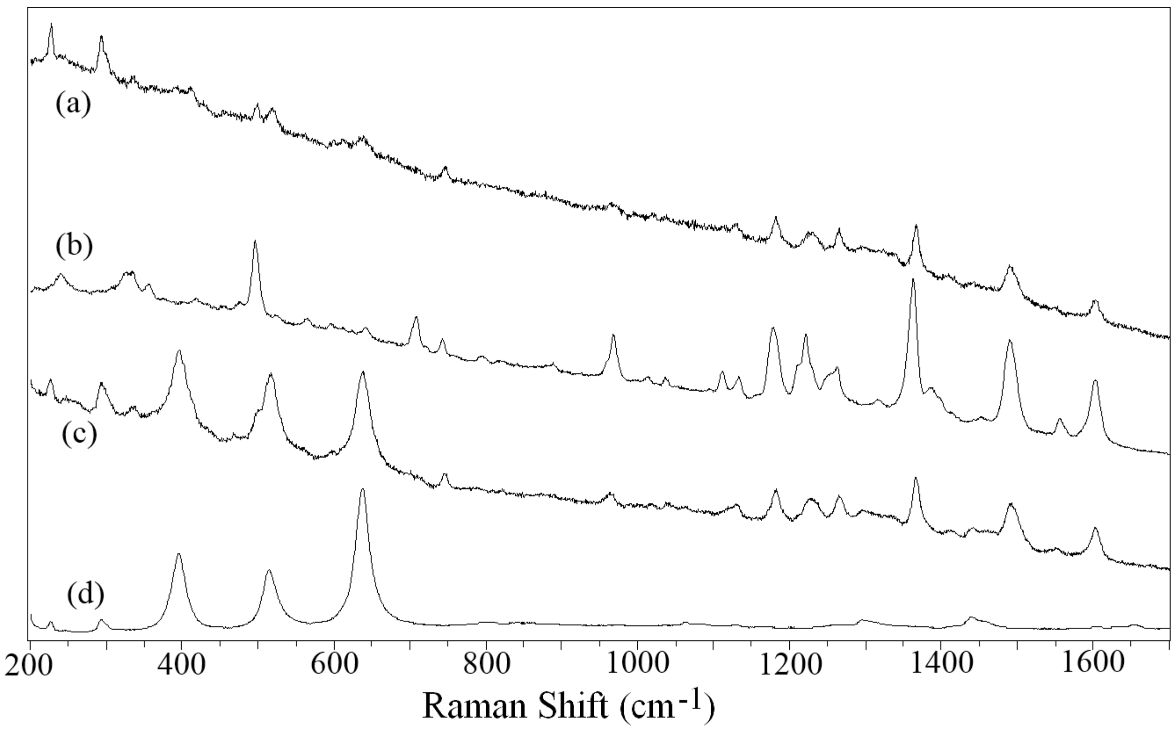

Fig. 1. Raman spectra of lipsticks (a) L'Oreal 524 (b) La Femme 29 (c) Revlon 075 (d) Barry M 101

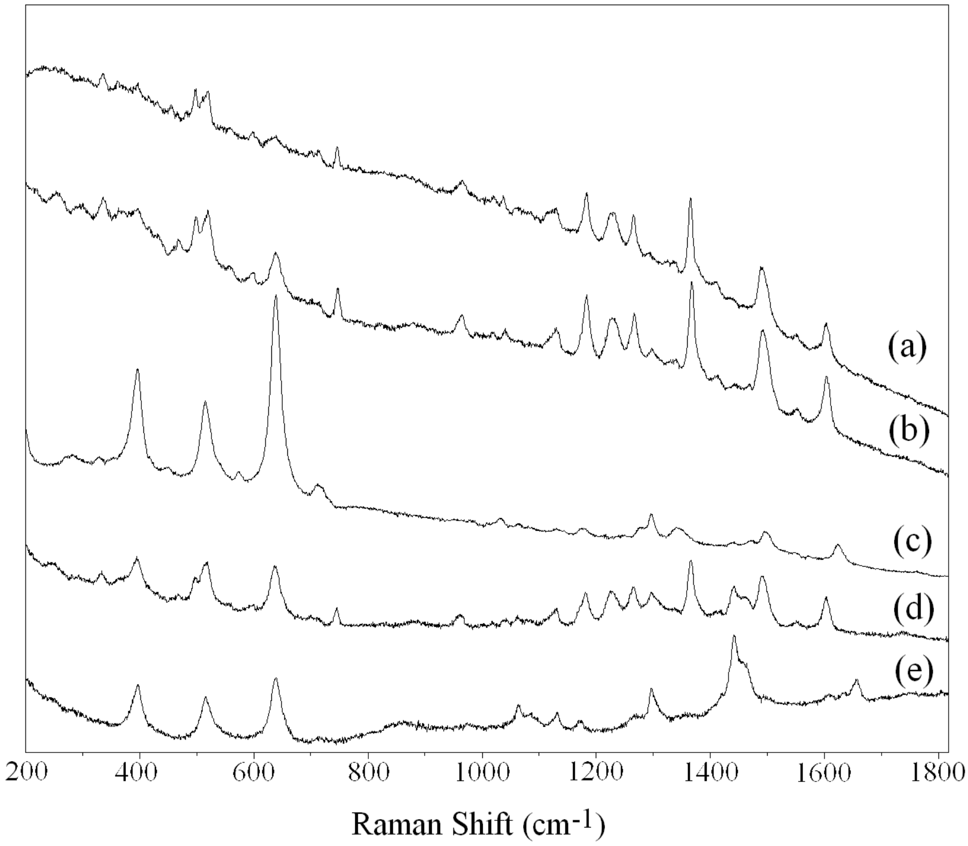

Fig. 2. Raman spectra of the pink lipsticks (a) Bourjois 15 (b) Revlon 025 (c) Barry M 52 (d) Revlon 020 (e) Barry M 113

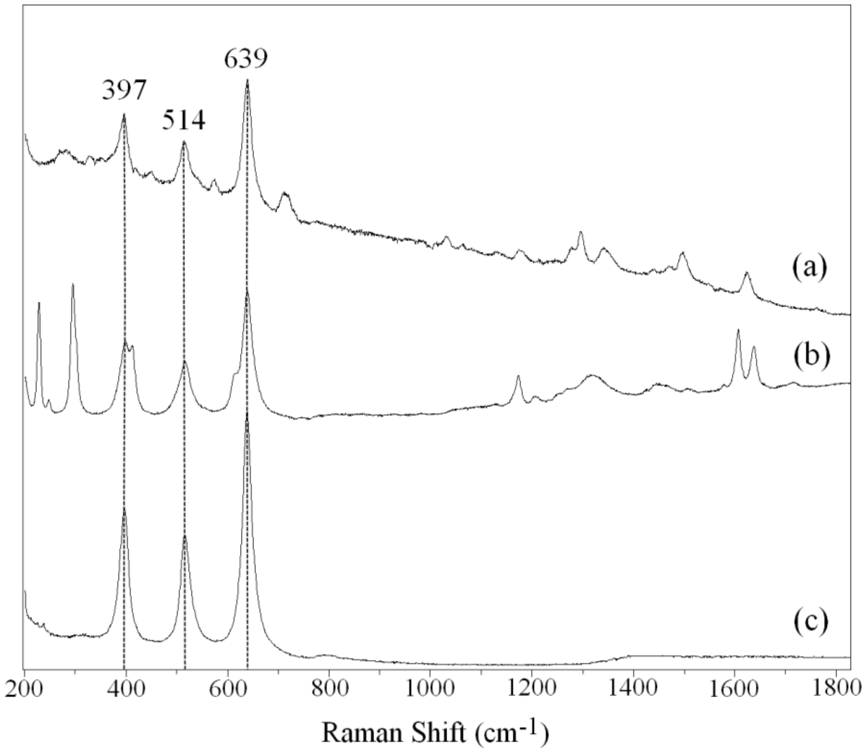

Fig. 3. Comparison of the Raman spectra of (a) Barry M 52 lipstick (b) Revlon 07 lipstick with (c) Titanium (IV) oxide (anatase form)

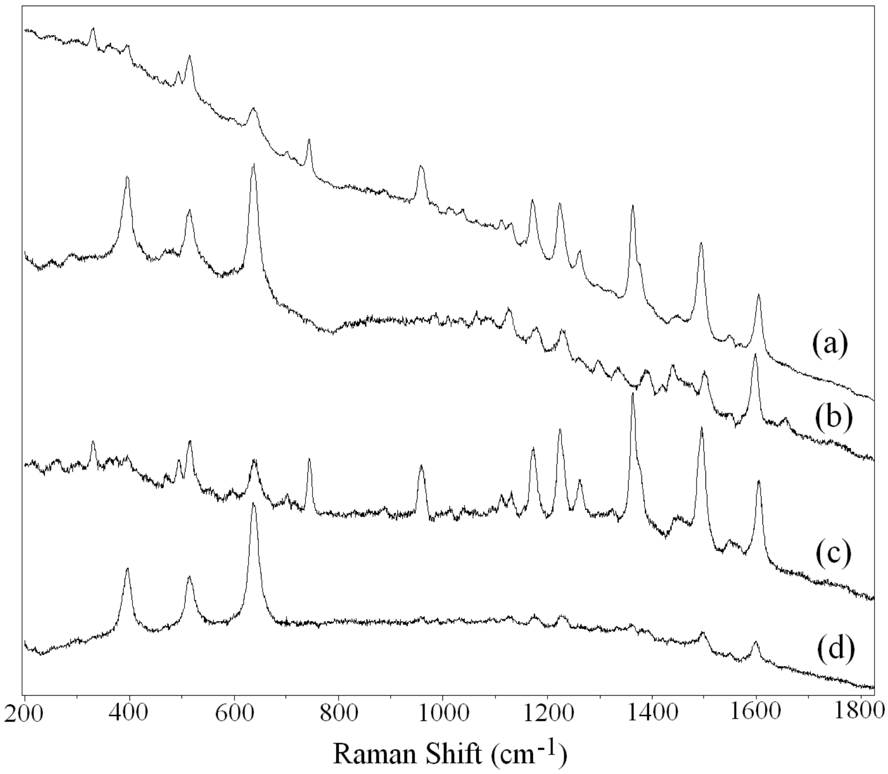

Fig. 4. Raman spectra of the orange lipsticks (a) Barry M 53 (b) Barry M 117 (c) Revlon 750 (d) Barry M 54

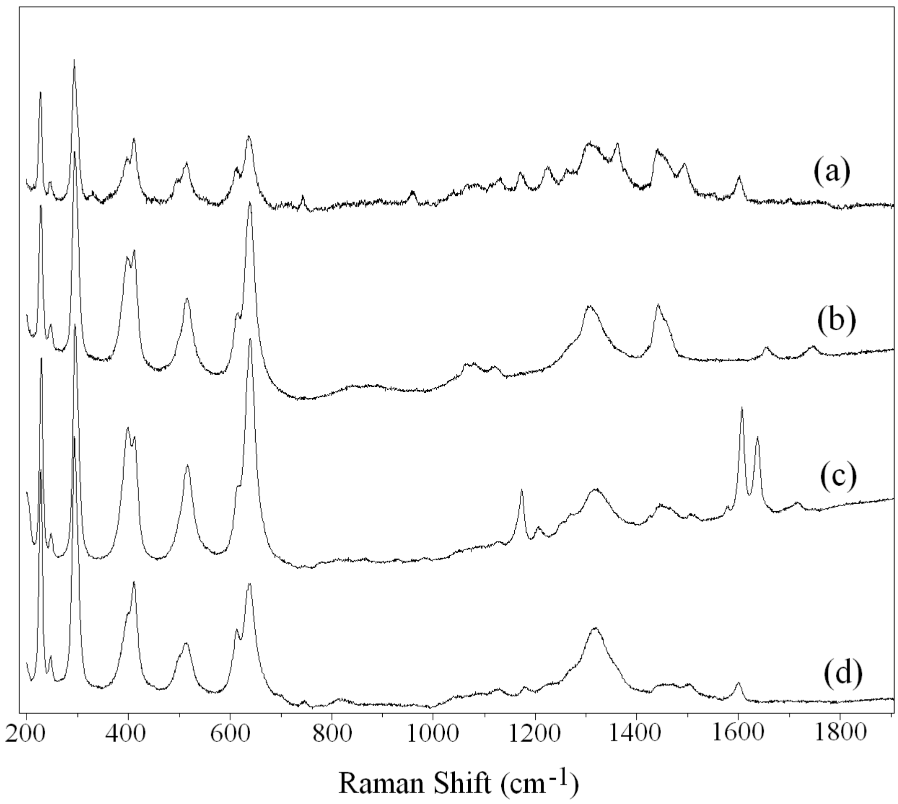

Fig. 5. Raman spectra of the brown lipsticks (a) Revlon 359 (b) UNE L02 (c) Revlon 07 (d) Revlon 008

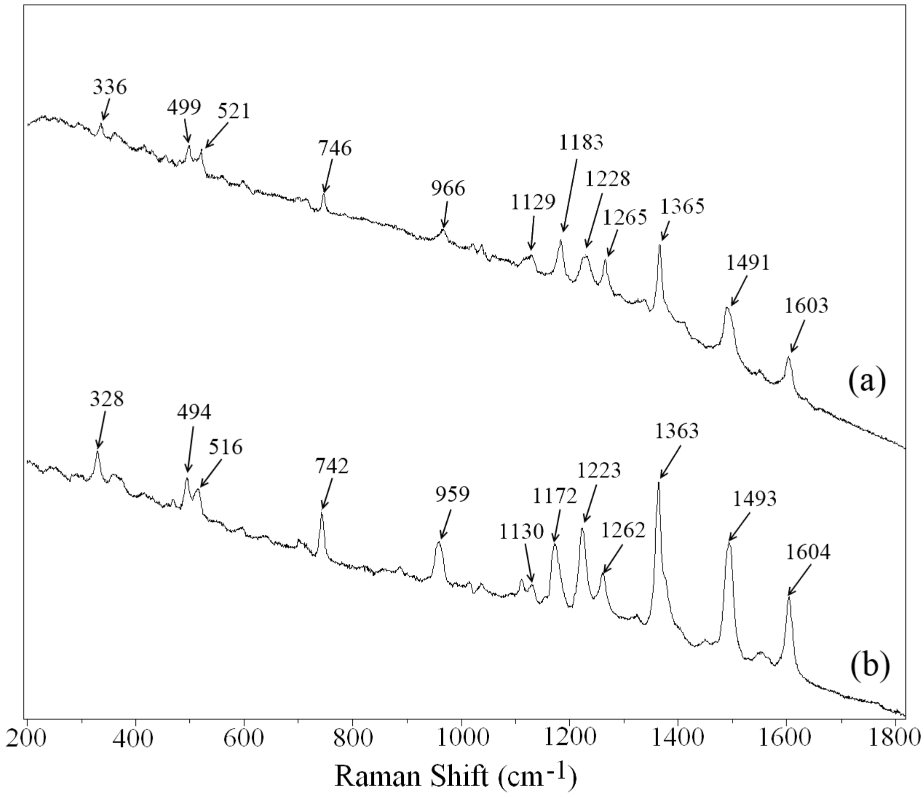

Fig. 6. Raman spectra of the red lipsticks (a) Bourjois 16 and (b) Revlon 080

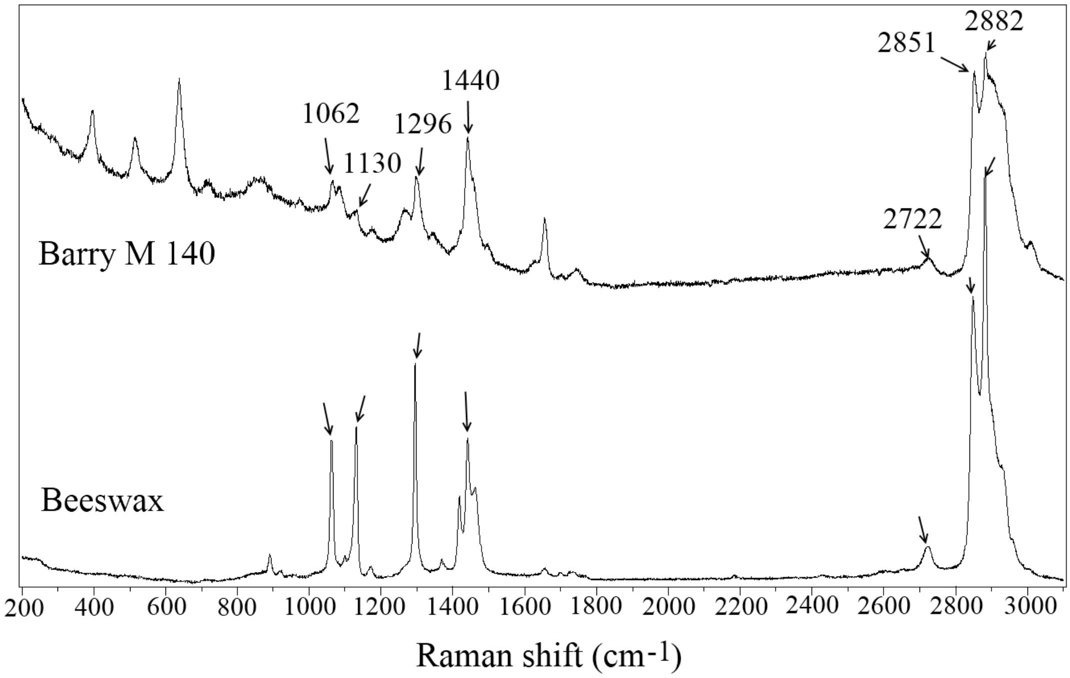

Fig. 7. Comparison of the Raman spectra of Barry M 140 and beeswax

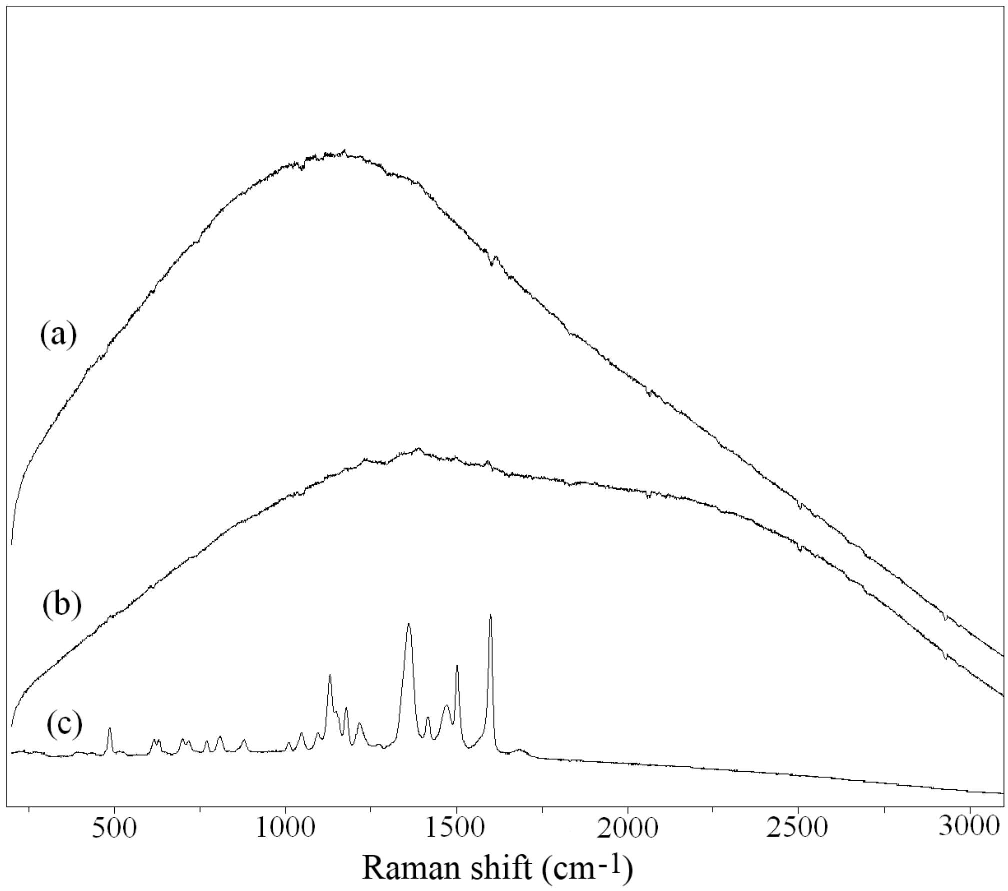

Fig. 8. Raman Spectra of (a) FD&C Blue No.1 (b) FD&C Yellow No.6 aluminium lake (c) FD&C Yellow No.5 aluminium lake

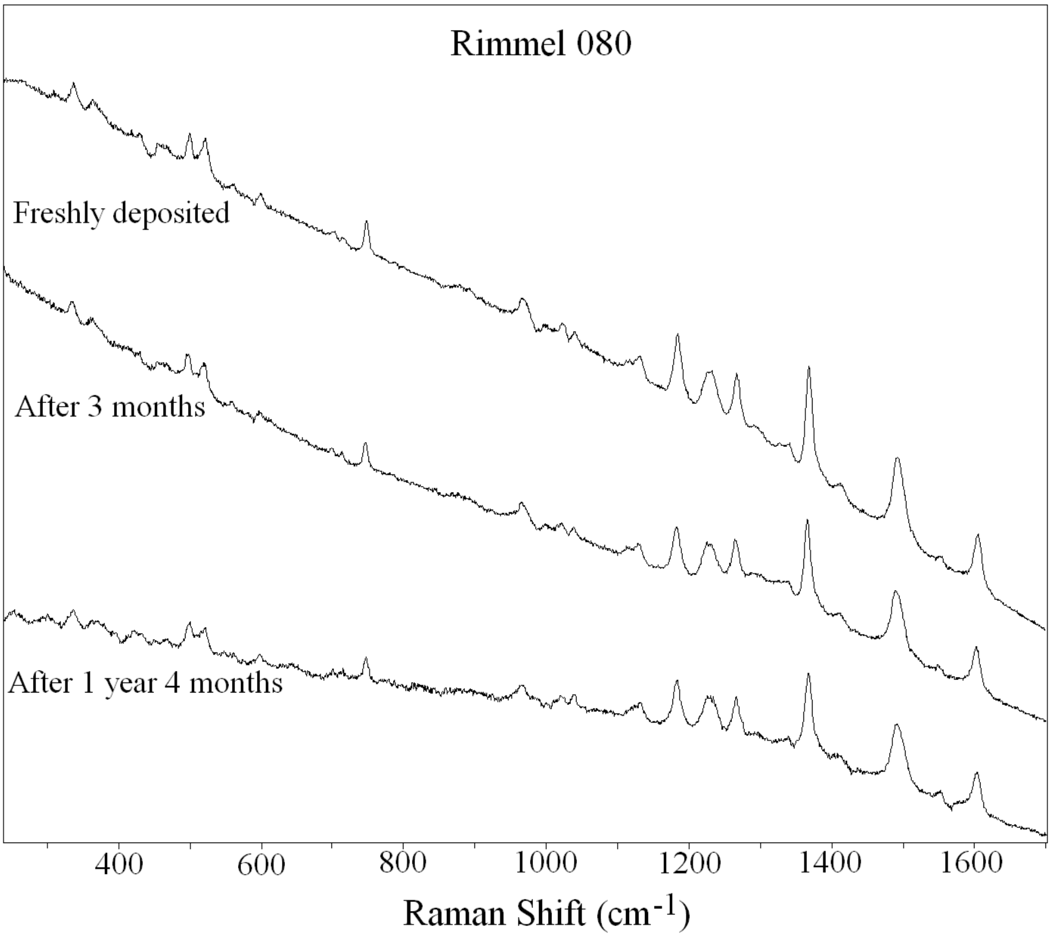

Fig. 9. Raman spectra of Rimmel 080 lipstick